Passenger tires inflated with nitrogen age slower

By John M. Baldwin, David R. Bauer and Kevin R. Ellwood
Ford Motor Co.

Nitrogen inflation is common to several industries. The aerospace industry uses nitrogen because of its consistent inflation pressure retention and reduction of oxidation in the rubber compounds. Auto and motorcycle racing use nitrogen because it is inherently dry compared to compressed air. Depending on the humidity of the inflation air, tire pressure can change dramatically (and non-linearly) during the heat build caused by racing. Nitrogen performs predictably as an ideal gas because it does not readily absorb or carry water. Large tires used on off-road vehicles in the mining industry, for example, use nitrogen to prevent auto ignition of the tires due to the high temperatures and thick treads.

Adoption of nitrogen tire inflation into passenger and truck tires has been much slower. Some reasons for the slower adoption rate of nitrogen inflation into mainstream applications are: 1. accessibility to nitrogen inflation systems, 2. cost of nitrogen inflation systems, both to the provider and the user, and 3. dearth of information as to the benefits of nitrogen inflation for either the fleet owner or average consumer. One benefit of using Nitrogen is claimed to be higher air pressure retention because of the lower permeability of Nitrogen than Oxygen. Higher NR and SBR compounds. While this is true in controlled laboratory tests of pressure retention in tires, the benefit to the real world consumer could be somewhat less. Pressure loss due to leakage around the rim flange seal of the tire to the rim and also the valve seal to the wheel (plus pressure loss through the valve itself) could account for some of the air loss experienced by the typical consumer, for example. It has been shown that nitrogen in a tire will result in a more even air pressure distribution in the tire. Further, the characteristic linear volume expansion with temperature because of nitrogen’s inherently low water absorption characteristics is no better to the average driver because the handling requirements for daily commuting are nowhere near as demanding as for racing; the improvement would be negligible and imperceptible.

The expected improvement in structural durability due to a significant reduction in rubber oxidation, however, could be a tremendous benefit to both the fleet owner and consumer. It is believed that rubber oxidation in the interior of a tire is caused by air from the cavity being forced into the tire carcass. The National Highway Traffic Safety Administration recently completed a study into the physical and chemical properties of field aged tires, including the mechanism of aging. The NHTSA study included "cut tire" analysis of approximately 150 tires retrieved from the field manufactured by Bridgestone/Firestone, Goodyear and Michelin. From the study:

"The general pattern of change indicates that cross-link density evolution due to aerobic and thermal aging is the dominant aging factor."

The tires that were the focus of the NHTSA study were found to be defective in part because the physical properties of the rubber in the steel belt area had deteriorated due to oxidative aging. Studies conducted by this laboratory confirm the NHTSA findings. Further work has demonstrated that accelerated oxidative aging of tires can be accomplished by use of an oxygen and the mechanism of aging is identical to that of tires obtained from the field. If the use of nitrogen as the inflation media can slow down or retard the oxidative degradation of tire rubber, then the durability of the tire should be improved. One mechanism for how tire durability could be improved is by reducing the oxidative aging of the wedge rubber.

The wedge rubber in a steel belted radial tire is added to help prevent belt edge separations from occurring. It is for this reason that the wedge rubber is one of the most important tire components; the wedge rubber helps determine the durability of a tire. As a tire goes... See Nitrogen, page 16

Fig. 1. Tire nomenclature used in this paper.

Anatomy of a Typical Radial Tire

Tread

#2 Steel Belt

#1 Steel Belt

Skim Stock (bond between belts)

Wedge

Fig. 2. Data analysis ("Ahagon Plot") used to understand aging mechanism of wedge rubber. The plot is of the log of the strain ratio at break vs. the log of the modulus at 100 percent strain. Linear Type I aging is considered normal oxidative aging. Type II aging is considered high temperature, anaerobic aging. The mechanism for Type III is high temperature oxidative aging, which also could be called diffusion limited oxidation (DLO).
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through repeated stress cycling during its lifetime, the strains are the greatest at the belt edge. When the wedge rubber aerobiologically ages, the material begins to stress harden. This stress hardening lowers the elongation at break and may lower its resistance to crack growth during the stress cycles. This is important because tread and belt delaminations start with cracks growing from the wedge inward between the steel belts. Nitrogen inflation could prevent the wedge from stress hardening, thus improving the crack growth resistance, which in turn would improve tire durability. Earlier work done on tube-type bias ply tires and radishoval tested steel-belted radials has shown improvements in durability compared to air-inflated tires.7

The research presented in this paper will concentrate on the effect nitrogen tire inflation has on the change in rubber properties around the steel belt of the tire. Tires inflated with 96 percent and 99.9 percent nitrogen were oven aged at 60°C for three to 12 weeks. For comparison, tires inflated with either air or a 50/50 mixture of N2/O2 were oven aged alongside the nitrogen-inflated tires. After aging, tires were cut and a number of tests were performed. These included the measurement of peel force between the first and second steel belt, which is a measure of the tearing energy of skim rubber. Tensile and elongation properties also were obtained from samples of the wedge rubber located between the steel belts in the shoulder.

Experimental

Materials

One tire type was used in the study, a Goodyear Wrangler AP LT245/75R16 (DOT Code: MD1APFWY0660). Tires were mounted and inflated to the maximum pressure listed on the sidewall prior to oven aging (450 kPa (65 psi)). In the case of tires inflated with the 50/50 blend of N2/O2, the atmospheric air pressure present was not purged; the blend was added on top of it. Yielding a tire cavity concentration of approximately 44 percent O2. For tires inflated to 96 percent nitrogen, 99.9 percent pure nitrogen was added on top of the atmospheric air present in the tire cavity, thus yielding the 96 percent concentration. The tires yielding 99.9 percent pure nitrogen cavities were inflated and purged 10 times each with 99.9 percent nitrogen. Tires were aged in the same oven for three, six, nine, and 12 weeks at 80°C. New tires were analyzed unaged and used as the baseline condition. The ovens were calibrated per ASTM E 145 with an ASMA approved, modified method for temperature uniformity, consistency, air flow exchanges and airflow velocity.

Physical properties

Tensile and elongation—Samples of the belt wedge rubber (Fig. 1), located between belts 1 and 2 were removed from both shoulders of unaged and aged tires and buffed to a uniform thickness of 0.5 to 1.0 mm. Care was taken so that no significant heat was transferred to the samples by the buffing. Samples were die-cut using an ASTM D 688 Type V dumbbell die and tested per ASTM D 412. Results obtained included stresses at 25 percent, 50 percent, 100 percent strain and each 100 percent strain thereafter, ultimate elongation and tensile strength. Samples were tested at 2.0 inches per minute (50.8 cm/minute).

Peel strength—Samples were prepared by cutting 2.5 inch (63.5 mm) wide radial sections, beads to bead. The sample was then sectioned into two 1.25 inch (31.75 mm) radial strips, which were each cut circumferentially at the centerline of the tread, resulting in four test specimens (2 SS and 2 OS). Each sample was cut with a razor knife for a length of 1 inch (25.4 mm), from the shoulder edge of the test strip, midway between the belts, to facilitate gripping the ends in the T-2000 Stress/Strain Tester jaws. The sides of each specimen were scored midway between the belts, to a depth of 1/8 inch (3.175 mm) radially from the end of the gripping surface to the end of belt 2 in the shoulder area, providing a 1 inch wide peel section. The peel test was performed at 2 inches per minute (50.8 cm/minute) at 24°C.

Reconstruction of skim and wedge rubber chemical formulation—An attempt was made to reconstruct the formulation. As the reader is undoubtedly aware, chemical reconstruction of a thermoset rubber is difficult and the precise formulation is known only to the compounder. Nevertheless, it is important to understand, at least generally, the chemical makeup of the compound one is studying. Table 1 contains the results.

Fig. 3. Ahagon plot for tires oven aged at 60°C with air, 50/50 N2/O2, 96 percent nitrogen and 100 percent nitrogen as the inflation media. The tires inflated with more than 95 percent nitrogen do not appear to change very much from the new tires, even after 12 weeks in the oven, whereas tires inflated with the oxygenated media change dramatically, even after three weeks in the oven.

Fig. 4. Normalized strain at break vs. time for tires oven aged at 60°C with air, 50/50 N2/O2, 96 percent nitrogen and 100 percent nitrogen as the inflation media. Again, tires inflated with more than 95 percent nitrogen do not appear to change very much from the new tires. The exception is the data for tires inflated with 96 percent nitrogen. The beginning of oxidative degradation can be seen. Nitrogen-inflated tires, however, degrade far slower than tires inflated with the oxygenated media.

Fig. 5. Normalized peel strength vs. time for tires oven aged at 60°C with air, 50/50 N2/O2, 96 percent nitrogen and 100 percent nitrogen as the inflation media. The results show that tires inflated with more than 95 percent nitrogen degrade at a much slower rate than tires inflated with air or 50/50 N2/O2.

Fig. 6. A graph of the normalized peel data whereby the data for tires inflated with the oxygenated media are shifted along the x-axis to show a close fit with data from tires inflated with more than 95 percent nitrogen. The data shifts overlap and appear to have an excellent fit to a logarithmic regression. This fact suggests that the change in the peel strength for nitrogen inflated tires is caused by oxidation in the skin rubber, not by changes in the crosslink distribution.
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constructed formula. It appears that the
skim and wedge compounds for this tire
construction are the same. It is also im-
portant to realize that the formula re-

presents the rubber as tested, not neces-
sarily as formulated.

Results and discussion

As stated in the introduction, the
wedge rubber is one of the most im-
portant components of the tire construction
related to durability. One of the more
useful ways to analyze the change in
properties of the wedge rubber is to uti-
lize the data analysis method of Atogun
and co-workers, which correlates the
strain ratio at break with the modulus
at 100-percent strain.

This approach is particularly useful in
distinguishing between different aging
mechanisms. By plotting the log of the
strain ratio at break vs. the log of the
modulus at 100-percent strain, a straight
line with a slope of -0.75 is indicative of
the aerobic aging of rubber. This ap-
proach was arrived at by taking one com-
pound with different levels of sulfur and
measuring the stress-strain data. The
same compound (at one level of sulfur)
was then oxidatively aged and it was
shown that the stress-strain data be-

haved identically to the compounds with
increased sulfur. Thus, the mechanism
of oxidative aging was inferred to consist of
increased crosslink formation. High tem-
perature aerobic (defined as Type III ag-
ing) or possibly anaerobic aging (defined
as Type II aging) of the rubber results in
data deviating from the straight line.

It is important to realize that the slope
of -0.75 is an empirically derived number
and more than likely dependent on the
aging characteristics of the individual
compound being studied. Careful reading
of the referenced studies does not yield a
"first principles" reason for the slope to
be any particular value. Fig. 2 is a repre-
sentation of how data for the various age-
ing types would look in graphic form.
Aerobically aging NR typically stress
dhardens, leading to lower elongation,
which yields a prediction of a negative
slope, given the data treatment shown.

Fig. 3 shows the results for the tires in
the present study plotted in the manner
described above. The nitrogen concen-
trations in the tire cavity at the beginning
of oven aging for the four filling gas con-
ditions were in ascending order: 56 per-
cent (the 50/50 N2/O2 inflation blend with
1 atmosphere of air present), 78 percent
(air inflation), 96 percent (99.9 percent
nitrogen with 1 atmosphere of air pre-
sent), and 99.9 percent (99.9 percent ni-
trogen with the 1 atmosphere of air
purged). The tires were aged at 60°C for
two to 12 weeks. As can be seen in Fig.
3, the wedge rubber of the tires contain-
ing more than 95 percent nitrogen expe-
rienced almost no change in stress-strain
properties, even after 12 weeks in the
evans, while tires filled with air or 50/50
N2/O2 experienced a substantial change
after only three weeks of oven aging. The
changes seen in the data for tires inflat-
ed with more than 95 percent nitrogen
are consistent with completion of curing
of the new tire, not oxidative aging. The
excluded points on the graph are for tires
with air and the 50/50 N2/O2 mixture at
12 weeks in the evans. The mechanism of
aging has been affected by loss of oxygen
due to permeability over that time and
the oxidation of the wedge rubber has
ever become limited by diffusion.

An additional method used to analyze
the data was to plot the normalized
strain ratio at break vs. residence time
in the evans at 60°C (Fig. 4). Normal-
ized strain ratio at break is determined
by dividing the strain at break of a tire
aged in the oven for time (t(oe)) and di-
viding it by the strain at break for a new,
unaged tire (t(0)). The results in
Fig. 4 show that for tires inflated with
more than 95 percent nitrogen there is
an initial drop in strain at break. The
reason for that again could be that new
tires generally are undercured and the
continuation of cure was completed dur-
ing the first three weeks in the oven.

After the first three weeks, the results
are unchanged for the durations tested,
except for the point at 12 weeks oven
duration and 96 percent nitrogen con-
centration. It may be that the oxygen con-
centration present in the tire took too
long to reach the wedge in concentra-
tions large enough to affect the strain at
break properties. Again, tires filled with
air or 50/50 N2/O2 experienced a sub-
stantial change after only three weeks of
oven aging and continued that trend out
to 12 weeks.

One conclusion that is inescapable
from this initial work is that the oxida-
tion of the steel belt rubber truly is dri-
ven from the contained air pressure in-
side a normal passenger or light truck
tire. Granted, the rate of degradation
would be much higher if no butyl in-
nerliner were present, but the presence
of innerliner and antioxidant packages
only slows the rate of degradation, not
eliminating it.

Peel strengths of the steel belt com-
posites also were evaluated. The peel
strength is a measure of the force re-
quired to separate the two steel belts
in a simple way to measure testing
energy.1 Fig. 5 shows the results for the
normalized peel strength vs. log time.
Normalized peel strength is determined
by dividing the peel strength of a tire
aged in the oven for time (t(oe)) and di-
viding it by the peel strength for a new,
unaged tire (t(0)).

As opposed to the results for the
strain at break of material obtained
from the wedge region of the tire, the
peel strength of rubber from the much
thinner skin region does degrade with
time for all inflation media used in the
study. The results in Fig. 5 also show,
however, that the tires inflated with
more than 95 percent nitrogen degrade
at a much slower pace than tires inflat-
ed with air or 50/50 N2/O2. The fact that
tires inflated with either 96 percent or
99.9 percent nitrogen degrade almost
identically leads one to believe that ei-
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other oxygen is reaching the belt skin rubber from the outside of the tire so that the change in peel strength is due to a change in the crosslink density distribution not detected in the wedge material properties. Both mechanisms are being investigated and will be reported in future work. Oxygen uptake measurements are being taken on the skin stock to determine whether oxygen is reaching the area from another source and crosslink distribution measurements are being made to determine if any sulfur rearrangements have occurred.

The data shown in Fig. 3, however, all appear to be changing according to the same mechanism. If that is true, then one should be able to shift the data according to a time-pressure superposition method to determine the acceleration of the degradation mechanism present. Ferris has shown that ultimate properties can be analyzed using reduced variables and shifted with respect to temperature or pressure. 23 In this case, the partial pressure of oxygen is different between the four conditions analyzed.

Fig. 6 is a graph of the normalized peel data whereby the data for tires inflated with air or 60/40 N2/O2 are shifted along the x-axis to line up with data from tires inflated with 100 percent nitrogen. The data shifts overlap and appear to have an excellent fit to a logarithmic regression. This fact suggests that the change in the peel strength for nitrogen-inflated tires is caused by oxidation in the skin rubber, not by changes in the crosslink distribution. One could infer from the shift factor between air and nitrogen inflation that tires inflated with nitrogen would take twice as long to deteriorate as air-inflated tires would. While this may be true at 60°C, the magnitude of improvement may be lessened if the data were shifted down to temperatures that tires operate at normally. The discrepancy would be caused by possible diffusion limited oxidation effects at 60°C vs. ambient temperature. The concentration of oxygen diffusing into the tire may be sufficiently low enough in the oven so that it never reaches the wedge and only small amounts reach the skin because at elevated temperatures the oxygen reactivity is increased. At ambient temperature, however, more oxygen may reach the skin and perhaps even reach the wedge. This is not to say that tire oxidation is not driven by the inside air pressure, just that in the absence of inside air pressure, oxidation in the wedge and skin regions may occur from outside air and the rate could be higher than what is reported at 60°C. Nontheless, it is perhaps a fair assumption to say that there would be some improvement in tire durability if nitrogen was used as the inflation media, but it is too soon to speculate as to how much of an improvement it would be.

Conclusions

The overall conclusion of the study is:

When N2 is used as the inflation media, the change in rubber properties is slowed down significantly or even halted. From a practical standpoint it is important to note that the presence of 1 atmosphere of air in the 80 percent nitrogen-inflated tires did not significantly affect the results, as compared to the 99.9 percent nitrogen-inflated tire. This is important for the average consumer because the need to purge existing tires completely of air before filling with nitrogen may not be necessary.

Another conclusion is that the oxidation of the steel belt rubber is driven from the contained air pressure inside a normal passenger or light truck tire. The skin region is oxidized slightly from outside the tire when filled with nitrogen, but the rate of degradation is significantly lower when the tire is filled with air. The wedge rubber, on the other hand, is in a sufficiently thick part of the tire and is not nearly as susceptible to oxidation from the outside.

The converse of this conclusion, therefore, is that oxidative aging can be controlled by the use of oxygen enriched filling gases in the tire cavity without changing the mechanism of degradation in the tire's internal components.

References

6. L.H. Kimball, Rubber Age, 89 (41), 89 (1967).

Presented at a meeting of the ACS Rubber Division, held May 17-19 in Grand Rapids, Mich.

Table I. Chemical reconstruction of the wedge rubber compound used in the tires used in this study.

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>PRH</th>
<th>Extractables</th>
<th>Ash</th>
<th>Volume</th>
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<td>Polyisoprene</td>
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<td>107.5</td>
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<td>Carbon Black (N326)</td>
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<td>1.0</td>
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<td>Zinc Oxide</td>
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<td>1.2</td>
<td></td>
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<td>Calcium Carbonate</td>
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<td>1.0</td>
<td>0.4</td>
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<td>Diocetyl Adipate</td>
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<td>1.0</td>
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<td>Sulfur</td>
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<td>12.8</td>
<td>7.8</td>
<td>157.2</td>
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Calculated Ash Content (by wt.) 4.2%  
Calculated Extractables (by wt.) 6.5%  
Calculated Carbon Black (by wt.) 33.1%  
Calculated Density (mg/ml) 1.173  

* Formulation may contain processing aids, waxes, etc.